

Anion Exchange Membrane Water Electrolysis: The Future of Green Hydrogen

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Cite This: *J. Phys. Chem. C* 2023, 127, 7901–7912



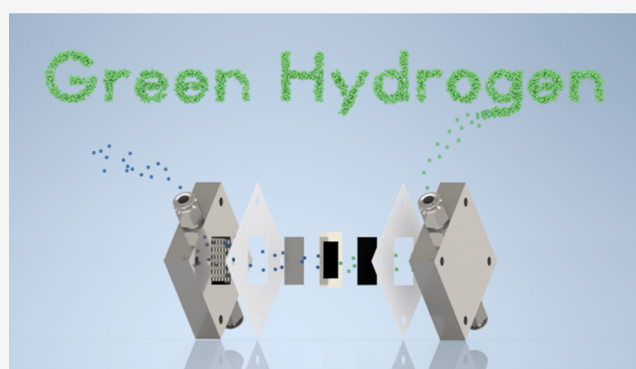
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ABSTRACT: Hydrogen-derived power is one of the most promising components of a fossil fuel-independent future when deployed with green and renewable primary energy sources. Energy from the sun, wind, waves/tidal, and other emissions-free sources can power water electrolyzers (WEs), devices that can produce green hydrogen without carbon emissions. According to recent International Renewable Energy Agency reports, most WEs employed in the industry are currently alkaline water electrolyzers and proton-exchange membrane water electrolyzers (PEMWEs), with ~200 and ~70 years of commercialization history, respectively. The former suffers from inherently limited current densities due to inevitable gas crossover, operates using corrosive (7 M) alkaline solutions, and requires large installation footprints, while the latter requires expensive and scarce precious metal-based electrocatalysts. An emerging technology, the anion-exchange membrane water electrolyzer (AEMWE), seeks to combine the benefits of both into one device while overcoming the limitations of each. AEMWEs afford higher operating current densities and pressures, similar Faradaic efficiencies when compared to PEMWEs (>90%), rapid ramping/load-following responsiveness, and the use of non-noble metal catalysts and pure water feed. While recent reports show promising device performance, close to 3 A/cm² for AEMWEs with 1 M KOH or pure water feed, a deeper understanding of the mechanisms that govern device performance and stability is required for the technology to compete and flourish. Herein, we briefly discuss the fundamentals of AEMWEs in terms of device components, catalysts, membranes, and long-term stability/durability. We provide our perspective on where the field is going and offer our opinion on how specific performance and stability tests should be performed to facilitate the development of the field.



INTRODUCTION

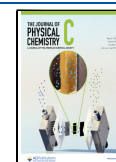
Reducing our dependence on fossil fuels is unprecedentedly urgent amid severe energy crises and accelerating global climate change. Nevertheless, assimilating/integrating renewable power sources requires grid-scale clean energy storage and transportation capabilities due to the daily, seasonal, and regional fluctuations of solar, wind, and tidal cycles. Hydrogen is an ideal energy carrier for building a global renewable energy system, as illustrated by its increasing use as a clean fuel. Hydrogen can be easily stored and transported in large quantities and utilized with high efficiency by fuel cells in cars, trucks, and even in small amounts in natural-gas infrastructures and turbines that operate on hydrogen. Unfortunately, 95% of the hydrogen in the world today is produced from natural gas reforming, a nonrenewable and highly carbon emitting process.¹ In fact, a simple analysis for hydrogen production from steam reforming of methane (ignoring the energy input

to drive the reaction) suggests a minimum of 5.5 kg of CO₂ produced for every 1.0 kg of H₂. Thus, to realize hydrogen as an alternative to fossil fuels, its production must be renewably sourced to yield green hydrogen. Water electrolyzers (WEs) represent one of the most promising solutions, as they can produce green hydrogen (assuming that the primary energy source is renewable and sustainable) from water without carbon emissions. Moreover, in addition to the benefits of using renewable hydrogen to displace fossil fuel-based sources,

Received: January 14, 2023

Revised: March 13, 2023

Published: March 28, 2023



proper operation of WEs themselves, when deployed with the overall energy system in mind, can improve the integration of renewable power and accelerate the transition to electrified transportation and other sectors. Electrolyzers operate by electrochemically splitting water into hydrogen at the cathode and oxygen at the anode ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2\uparrow + \text{O}_2\uparrow$), with ions being transferred between the two electrodes to maintain electroneutrality.

Currently, most WEs are alkaline water electrolyzers (AWEs), which employ a porous membrane as a separator—known as a diaphragm—and a highly concentrated liquid alkaline electrolyte (usually 25–30 wt % (ca. 7M) KOH).² The diaphragm does not effectively prevent gas crossover between the anode and the cathode, resulting in poor Faradaic efficiencies (especially at partial-load operation), improper drying of the hydrogen gas, and a limited range of operating pressures.³ In addition, hydrogen generated by AWEs usually requires additional stages of costly drying and compression since it is generated at near ambient pressure. For the same reason, AWEs cannot employ a very thin diaphragm to lower the ionic resistance without compromising the gas crossover and overall efficiency of the device. Thus, although high concentrations of KOH electrolytes (25–30 wt % KOH) are typically employed, the maximum current densities of AWEs are limited to about 0.2–0.4 A/cm².² In addition, these ultrahigh concentrations of KOH electrolytes introduce significant problems related to the corrosion of device components, which in turn increase the device balance-of-plant, and maintenance costs.

High-performance water electrolysis using pure water has been realized through proton-exchange membrane water electrolyzers (PEMWEs), utilizing polymer electrolyte membranes (usually <50 μm) to separate the gases while decreasing ionic resistance. PEMWEs can efficiently operate at current densities of >2 A/cm².⁴ However, the local acidic environment in PEMWEs, strictly limits the choice of electrocatalysts to a handful of platinum group metal (PGM) materials such as Pt, Pd, IrO₂, and RuO₂. Usually, Pt-based electrocatalysts are needed for the hydrogen evolution reaction (HER) at the cathode, while Ir- or Ru-based electrocatalysts are used for the oxygen evolution reaction (OER) at the anode.⁴ The high catalyst loadings, typically ~3 mg_{PGM}/cm², required to sustain significant current densities lead to high costs and severely hinder the large-scale application/deployment of PEMWEs. Furthermore, PEM-based electrolysis typically uses fluorinated membranes, such as Nafion, that make the recycling of the precious metal catalysts very complicated, as environmental regulations often prevent the fluoropolymers from being incinerated for catalyst recovery. Anion-exchange membrane water electrolyzers (AEMWEs) combine the advantages of both AWEs and PEMWEs while mitigating many of their drawbacks. Like PEMWEs, AEMWEs utilize a solid polymer electrolyte, an anion-exchange membrane (AEM), enabling high operating currents and pressures. Moreover, alkaline environments are much less corrosive than acidic ones and enable the utilization of less-expensive non-PGM catalysts, such as first-row transition-metal oxides, nitrides, and sulfides, making large-scale commercialization feasible.

In this perspective article, we focus on the basics of AEMWEs, the scientific and engineering progress made in recent years in the development of device components, and the challenges that lie ahead for the future of AEMWE development. We discuss the importance of developing efficient and

stable non-PGM alkaline OER electrocatalysts, understanding the OER reaction mechanisms, and developing stable alkaline polymer electrolytes (APEs) with high ionic conductivity, especially at high current densities, mechanical strength and chemical stability. Finally, we summarize the recent realization of high-performance AEMWEs working with pure water or “dilute” KOH (compared to AWEs) and our outlook on the field.

■ BASICS OF AEMWEs

The essential structure of an AEMWE is shown in Figure 1. Located in the center, a thin AEM (usually <50 μm in

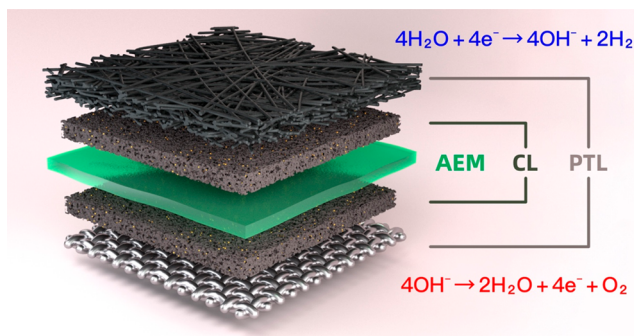


Figure 1. Schematic diagram showing critical components of an anion exchange membrane water electrolyzer (AEMWE), including the alkaline exchange membrane (AEM), the catalyst layers (CLs), and the porous transport layers (PTLs). The flow field plates are omitted for clarity. Figure not drawn to scale.

thickness) serves as a gas-impermeable “separator” of the two electrodes and cell compartments as well as the cationic polymer electrolyte that enables the transport of hydroxide anions from the cathode to the anode. Thus, good chemical and mechanical properties and high ionic conductivity are required. The catalyst layers (CLs) consist of HER and OER—cathode and anode, respectively—catalysts, usually prepared on a support, both embedded in an ionomer, serving as both an anion conductor and catalyst binder. Although the AEM and ionomer can be different APEs, combining different APEs can be impractical if the ionomer does not properly adhere to the AEM, resulting in interfacial resistances and incompatibilities that can (and often do) compromise electrolyzer performance. Finally, surface-treated metal foams or felts serve as porous transport layers (PTLs) to provide mechanical support while promoting the transport of gases and liquids at both electrodes. A microporous layer between the PTL and the CL can be used to achieve better electrical contact. Surface-treated metal plates can be used as bipolar plates (not shown in Figure 1), and the generated gases can be discharged from the device through additional outlets.

Carbon-supported PGM HER electrocatalysts are usually employed at the cathode, and the CL can be directly coated onto the membrane. However, PGM HER catalysts can be readily substituted in the alkaline system by Ni-based electrocatalysts.⁵ While they are less active than PGM catalysts when normalized to volume or surface area, similar overpotentials can typically be achieved through higher loadings at a fraction of the cost (Ni is currently 1000 times less expensive than Pt).⁶ On the other hand, PGM Ir- and Ru-based OER electrocatalysts are generally the highest performing anodes.

Similar to the HER at the cathode, non-PGM electrocatalysts, such as Ni-Fe-based materials,⁵ can be employed as OER catalysts at the anode to considerably reduce costs (Ni is currently 8000 times less expensive than Ir).⁶ OER catalysts need to be either self-supported or supported on conductive metal oxides or nitrides because carbon corrodes at OER potentials, making the dispersion of OER catalysts in typical solvents such as EtOH or iPrOH challenging. Thus, anode catalysts are often brushed onto the anode PTL instead of sprayed directly onto the AEM. The AEMWE performance is typically better when “dilute” electrolytes are employed (≤ 1 M KOH) as opposed to water, mainly due to the dramatically improved ionic conductivity. To a limited extent, this can also be achieved by using better ionomer binders. On the other hand, devices operating with pure water are preferred due to the system’s simplicity in chemical management and device maintenance.

For a WE system, the total energy required to produce a specific amount of hydrogen is crucial, as it correlates directly to its cost. The voltage efficiency of a WE cell at a specific current density can be calculated using the thermodynamic voltage for the water splitting reaction (1.23 V at 25 °C) divided by cell voltage, which does not take into account Faradaic efficiency. It can also be calculated by dividing the higher heating value (HHV) or the lower heating value (LHV) of hydrogen (3.54 and 3.00 kW·h/N·m³, respectively) by the electric energy consumed in the electrolysis. The HHV and LHV efficiencies are meaningful as they correlate directly to the efficiencies of an analogous internal combustion engine.

■ ALKALINE OER MECHANISMS

The complexity and overall sluggishness of the electrolysis of water calls for the development of better-performing HER and OER catalysts to lower the device energy consumption (overpotential). Regardless of pH, the OER kinetics are significantly slower than those of the HER. Therefore, progress in OER electrocatalysis is likely to directly translate into better device performance as long as the OER remains the rate-limiting half-reaction. Moreover, the “absolute” electrochemical potentials required to drive the OER can be corrosive on their own, a phenomenon that can be exacerbated by the presence of oxygen at the anode. Thus, better and more stable catalysts can also promote a less corrosive environment at the anode. So far, two main OER mechanisms have been widely proposed/investigated in the literature (Figure 2): the adsorbate evolution mechanism (AEM) and the lattice oxygen/oxidation mechanism (LOM).⁷ To avoid confusion with the identical acronym for alkaline/anion exchange membrane—also AEM—we recommend the use of the term *metal-site adsorbate evolution (MAE) mechanism*, as already employed by Zhou et al.⁸ In the former mechanism, the metal

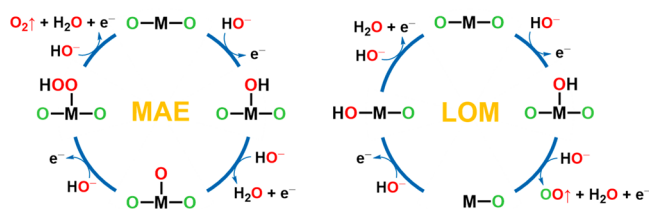


Figure 2. Metal-site adsorbate evolution (MAE) mechanism and lattice oxygen/oxidation mechanism (LOM) catalytic cycles.

centers directly bind oxygen, hydroxide, and the other intermediates associated with the evolution of oxygen, without the direct involvement of lattice oxygen. In the latter case, lattice oxygen ions at the heterogeneous interface are consumed to produce molecular oxygen, forming so-called lattice oxygen vacancies (V_{O}). The presumption behind the LOM being a proper catalytic process rather than an undesired degradation reaction producing molecular oxygen is that the transient oxygen vacancies formed during the reaction do not destabilize the local electronic structure at the interface and cause the dissolution of the metal centers. Put differently, any lattice oxygen ion “lost” to the formation of molecular oxygen must be replenished by solution species that, in turn, leave behind (replenish) a new lattice oxygen ion.

The above mechanisms and their general applicability are still contested, even for the same electrocatalyst. For example, studies showing a current density dependence on metal dissolution rates for polycrystalline RuO₂ and claiming that RuO₂ OER proceeds via LOM⁹ are contrary to those claiming that no lattice oxygen is involved in the process and, thus, a different reaction mechanism (MAE-type) must apply.¹⁰ These differences notwithstanding, both mechanisms require metal centers to effectively bind hydroxide and the other oxo species while also effectively releasing O₂. This defines the binding energies for the reaction intermediates, popularized in the literature by the scaling relationships of the so-called volcano plots.

■ ELECTROCATALYST PERFORMANCE

To achieve efficient OER catalysis for alkaline electrolysis, recent efforts have included noble metal catalysts, mainly PGM-based oxides and alloys,^{11–14} and non-noble metal catalysts, ranging from simple and scalable Ni-Fe hydroxide systems,¹⁵ to other oxides,¹⁶ sulfides,¹⁷ phosphides,¹⁸ and even highly sophisticated DNA-based¹⁹ three-dimensional (3D) catalysts. Extensive reviews on recent progress in electrocatalysts for alkaline OER can be found elsewhere.⁷ The overpotential needed to achieve a current density of 10 mA/cm² (η_{10}) has been widely used as a standard metric for catalyst performance following the approach used in photoelectrochemical energy conversion (current density expected for a 10% efficient solar-to-fuel device under one sun).²⁰ In the literature, one can find catalysts with a claimed η_{10} for the OER as high as >350 mV and as low as 32 mV.²¹ However, a lack of consistency in terms of catalyst mass loading, *iR*-correction use, and surface area normalization makes the comparison of η_{10} values among publications extremely unreliable. For example, the reported 65 mV η_{10} for a NiFe/S catalyst supported on Ni foam²² was not a measure of the OER Faradaic process but rather the double-layer baseline. Based on how problematic ECSA normalization is for non-PGM electrocatalysts, primarily when Ni foam (electrocatalytically active) is utilized as a support, we recommend that cyclic voltammograms (including both anodic and cathodic scans) be used as opposed to linear sweep voltammograms when comparing OER RDE polarization curves.

Figure 3a–c shows recently published polarization curves recorded for OER catalysts in 1 M KOH. Figure 3a summarizes data by Lee and co-workers obtained using graphitic-carbon-encapsulated CoFe₂ alloy nanoparticles decorated with single Ru atoms versus several reference catalysts.¹⁴ Their best catalyst achieved an η_{10} of 180 mV with just 2 wt % Ru (after an 85% *iR* correction),

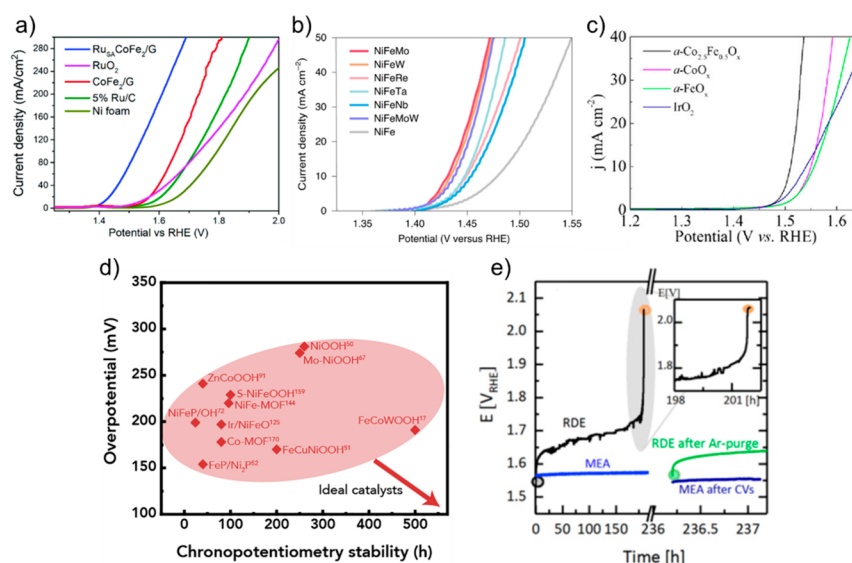


Figure 3. (a–c) Examples of OER polarization curves of (a) Ru-based, (b) Ni-Fe-based, and (c) amorphous Co-Fe-based catalyst systems. (d) Catalyst performance (η_{10}) plot, where the x -axis corresponds to the time associated with the CP exponential increase. (e) RDE and PEMWE CP stability tests for an IrO_2 catalyst; inset shows the very end of the RDE test. Panel (a) is reprinted with permission from ref 14. Copyright 2020 Royal Society of Chemistry. Panel (b) is reprinted with permission from ref 23. Copyright 2020 Springer Nature. Panel (c) is reprinted with permission from ref 24. Copyright 2022 American Chemical Society. Panel (d) is reprinted with permission from ref 7. Copyright 2021 Elsevier. Panel (e) is reprinted with permission from ref 31. Copyright 2021 The Electrochemical Society.

outperforming a commercial RuO_2 reference catalyst by 120 mV. However, significantly different double-layer capacitances and debatable post-OER characterizations obscure a reproducible interpretation of their results. Figure 3b shows the results by Zhang et al., who evaluated the effect of doping NiFe and FeCo catalysts with Mo, W, Re, Ta, and Nb to vary the Fe(II) content from 0 to 50% and found a direct correlation between the amount of Fe(II) and OER performance.²³ Their best-performing NiFeMo also exhibited an η_{10} of 180 mV, albeit with 95% iR correction. Separately, Zhang and co-workers explored amorphous Co- and Fe-based oxides as OER catalysts (Figure 3c). Their most active catalyst exhibited an η_{10} of 280 mV, with an unspecified iR correction,²⁴ demonstrating the viability of amorphous (as-prepared) materials made from first-row transition metals as promising AEMWE catalysts. But, since it is known that the catalyst structure, morphology, etc. can change during OER,²⁵ this type of catalyst would need to be carefully characterized after (or when possible, during) OER to reveal its true active form. Lastly, Figure 3d shows a plot of η_{10} as a function of apparent stability, taken from chronopotentiometric (CP) experiments with oxide, hydroxide, phosphide, and sulfur-decorated catalysts.⁷ The data in this figure attest to the frequently observed activity–durability trade-off in electrocatalysis.

Aside from a high-activity requirement (low η_{10} in an RDE cell), OER electrocatalysts must perform well in electrolyzer-type electrodes, where ink and film homogeneity are crucial. As demonstrated by Garsany et al. using commercial Pt/C films as oxygen reduction reaction (ORR) electrocatalysts in an RDE cell, the quality of the catalyst inks and the deposited catalyst films can have a significant effect on the overall electrocatalyst performance.²⁶ These effects are expected to be even more pronounced for OER catalyst films, where one of the reactants/products is an undissolved gas. Also, OER electrocatalyst layers must be highly conductive, as the iR -drop in a device operating at ampere-level current densities easily

surpasses those observed in RDE cells.²⁷ As a general rule, performing iR corrections in an RDE cell may conceal conductivity limitations, including the intrinsic catalyst resistance, as well as the substrate/catalyst and the catalyst/electrolyte interfacial resistances of nonideal systems with convoluted impedance responses. At the same time, over-reliance on iR -corrected data may misrepresent the viability of catalysts, as eliminating iR -drop resistances in real devices is not feasible.²⁸ For example, analyses of iR -overcorrected data sets in the literature, such as voltammograms with a negative slope at high current densities, would suggest unphysical catalytic responses.^{29,30} Therefore, we recommend that catalyst polarization curves not be iR corrected or that both corrected and uncorrected data sets be presented.

Lastly, we suggest that electrocatalysts should pass appropriate stability tests in AEMWE devices. As demonstrated by Tovini et al. in acidic media (Figure 3e), the microbubbles generated during OER tests using an RDE can get trapped at certain oxophilic catalyst layers and even at the surface of bulk electrodes.³¹ After minutes or hours of operation, these can electrically insulate catalysts such as IrO_2 , otherwise known to last years in a device, causing an increase in overpotential as high as 500 mV. This “degradation” mechanism is not observed in PEMWEs, which maintain a stable performance over much longer periods of time. Consequently, the widely used RDE CP experiments are not reliable for comparing the stability of OER catalysts for AEMWEs since not all films are oxophobic enough not to trap O_2 microbubbles.³² We thus postulate that only AEMWE stability tests, such as chronoamperometry (CA) at a cell voltage of 1.8 V for a minimum of 100 h, should be used for the reliable comparison of catalyst performance stability. The degradation rate, expressed in $\mu\text{A}/\text{h}$ or mA/h , should be used to compare OER catalyst relative stabilities, provided that a stable HER catalyst (e.g., Pt/C) is used at the cathode. However, since AEMWEs are much scarcer than RDE setups,

given the differences in complexity and cost, RDE OER CP stability test³³ may still be valuable as long as the catalyst film used does not trap microbubbles (*i.e.*, the performance is stable as a function of time).

■ AEMWE MEMBRANES

While APEs have been primarily explored for alkaline exchange membrane fuel cells (AEMFCs), more attention has recently been devoted to the application of these materials in AEMWEs. AEMs and ionomers are produced from APEs, which have a cationic functionality promoting the conduction of hydroxide ions with a polymer backbone providing mechanical integrity. The physical properties, chemical properties, and stability of APEs are thus influenced by the composition of the polymeric backbone and the cationic functionality. An extensive review of the synthesis of APEs can be found elsewhere.³⁴

The polymer backbones employed in APEs include polyaromatics like poly(arylene ether)s,³⁵ poly(arylene ether ketone)s, poly(arylene ether sulfone)s,^{36,37} polyphenylenes,^{38,39} polyfluorenes,^{40,41} and polyolefins such as polystyrene,⁴² polynorbornene,^{43–45} and polyethylene.^{46,47} The choice of the polymer backbone providing the mechanical scaffold for the cations dramatically influences the chemical and mechanical integrity of the resulting APEs. Parameters often considered when characterizing APE materials include thermal transition(s), solubility, and tensile strength. The thermal transitions of the polymer, such as the glass transition temperature (T_g) and the melting temperature (T_m), influence the polymer processability and mechanical integrity at AEMWE operating temperatures (60–80 °C). For example, polymers soluble in organic solvents can be solvent-cast to form thin films and are amenable to making ionomer solutions. At the same time, those with low solubilities must be processed by melt-pressing to form AEMs, making large area/thin membrane fabrication difficult. Additionally, the tensile strength of the polymer—both dry and wet—can inform its capacity for easy handling and assembly and not break upon swelling in the aqueous KOH solution.

The hydrophobic and mechanically strong polymer backbone supports the hydrophilic cationic functionality necessary for hydroxide ion conduction. Generally, higher initial ionic conductivities are observed for APEs with more cations or higher ion exchange capacities (IECs; $\text{mmol}_{\text{ion}}/\text{g}_{\text{polymer}}$). However, increasing the IEC of the material also increases water uptake,^{44,47} which may lead to mechanical failure and catalyst layer exfoliation due to polymer swelling. Balancing the IEC and mechanical properties of each polymer/cation system is critical for optimizing APE performance. If a membrane shows excessive swelling, cross-linking can help the APE retain its mechanical properties even at high IECs.⁴⁶

The presence of organized and cocontinuous microphase separation of the hydrophobic and hydrophilic regions of the polymer may also promote conductivity. However, additional research is needed to understand the relationships between/among microphase separation, polymer morphology, and the resulting APE performance. Techniques including multiblock copolymer synthesis,^{43,48} interpenetrating networks,⁴⁹ or adjusting the linker length between the backbone and the cation⁵⁰ have been employed to achieve specific polymer morphologies in APEs. While the physical properties of APEs must be considered to ensure good film formation and mechanical integrity, the chemical stability of the polymer

backbone under alkaline and oxidative conditions is crucial for the successful implementation of AEMWEs.

APEs employing backbones with heteroatom linkages, such as poly(arylene ether)s, poly(arylene ether ketone)s, and poly(arylene ether sulfone)s, should be avoided as they are prone to degradation by hydroxide attack via nucleophilic aromatic substitution (S_NAr) at the ether linkages (Figure 4a),

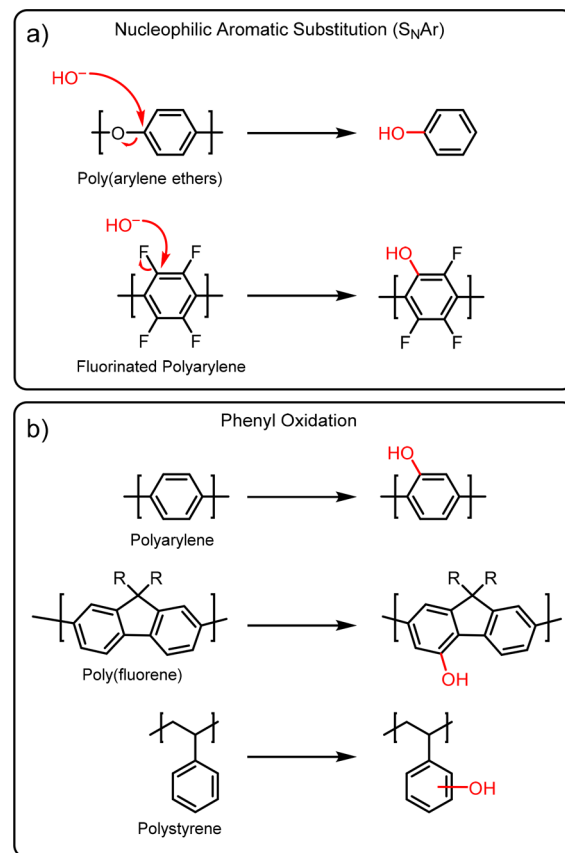


Figure 4. Polymer backbone degradation mechanism under alkaline and oxidative conditions. (a) Nucleophilic aromatic substitution (S_NAr) degradation mechanism observed for poly(arylene ether), poly(arylene ether ketone), poly(arylene ether sulfone), and fluorinated poly(arylenes). (b) Phenyl oxidation observed in APEs containing aromatic moieties.

which can lead to a reduction in molecular weight.⁵¹ Hydroxide can also attack fluorinated phenyl groups via S_NAr , in this case leading to phenol or aryl ether formation, which can result in cross-linking within the AEM.⁵² APEs containing aromatic groups can adsorb onto the electrocatalysts when used as an ionomer and “poison the catalyst”,⁵³ causing performance loss and degradation of the ionomer via phenyl oxidation⁵⁴ (Figure 4b), leading to further performance losses.⁵⁵ This overall degradation pathway is particularly prevalent in AEMWEs compared to AEMFCs as the AEMWE anodes operate at potentials significantly higher than those of AEMFC cathodes, facilitating the oxidation of phenyl groups in the ionomers.⁵⁶ Variations in the structure of the aromatic moiety can dramatically change the adsorption energy on the electrocatalysts.^{53,55} Thus, the performance and stability of aromatic APEs can be improved by employing aromatic groups with lower adsorption energies.⁴² Hence, we recommend that completely aliphatic APEs such as poly-

norbornenes and polyethylenes, which are more stable under alkaline and oxidative conditions, be used to avoid degradation via S_NAr and phenyl oxidation.

The physical properties and stability of the polymer backbone must be considered when designing long-lasting, high-performance APEs. Aliphatic polymers with either a high T_g or T_m and good film-forming and tensile properties are best suited to achieve the desired physical properties and stability. The ease of cation incorporation into the polymer is also an essential factor, as, without cations, there is no APE. The cationic moieties allow for the conduction of hydroxide through the APE by attracting hydroxide and inducing water uptake. The hydrophilicity, size, and stability of the incorporated cation will impact the resulting APE properties. Two methods are generally employed to incorporate cations into the polymer to form APEs: direct polymerization and postpolymerization functionalization. In direct polymerization, cation-functionalized monomers are polymerized to incorporate cations into the polymer. In contrast, in postpolymerization functionalization, a neutral polymer is subjected to subsequent reactions that transform a functional group on the polymer into a cationic unit. In most cases, direct polymerization is preferable as it allows more effective incorporation of a wider variety of cations in high concentrations.

Cations incorporated into APEs include but are not limited to quaternary ammoniums,^{38,44} imidazoliums,⁴⁶ and phosphoniums.⁴³ Trimethylammoniums are the most common type of cation employed in APEs as their incorporation into polymers is facile, and their small size allows for the highest maximum IEC. Nevertheless, achieving long-term alkaline stability of the cations within APEs is still the main challenge for these materials. The interested reader can look at an extensive review by Yang, Peltier et al. that covers rates and mechanisms of degradation of organic cations employed in APEs.⁵⁷

Quaternary ammoniums can degrade by nucleophilic substitution (S_N2) and elimination (E2) (Figure 5a).⁵⁸ S_N2 attacks are most prevalent at benzylic positions, which are common tethering points when appending ammoniums onto aromatic backbones. Thus, quaternary ammoniums with a benzylic position should be avoided in the interest of the long-term chemical stability of APEs. Additionally, E2, also known as Hofmann elimination, may occur when there are β -hydrogens antiperiplanar to the nitrogen in the ammonium group. Piperidinium-based cations tend to be the most stable of the ammoniums as the low ring strain makes ring opening by S_N2 or E2 less favorable.⁵⁹ Recently, more APEs employing piperidinium have been explored, as piperidiniums effectively achieve a good balance among stability, synthetic feasibility, and conductivity.^{38,47,60}

While penta-substituted imidazoliums are very stable, their unsubstituted counterparts degrade rapidly.^{58,61} Nucleophilic addition at the C2 position (Figure 5b) is the most common degradation mechanism for imidazoliums. These can also undergo deprotonation at the C-4/5 positions and S_N2 attack of the N-1/3 substituents, which is why imidazoliums need substituents at all five positions of the ring to achieve long-term alkaline stability.⁶¹ Similarly, tetrakis-aminophosphoniums are extraordinarily stable, especially when functionalized with bulky substituents on the amino groups.⁶² Extra-harsh alkaline conditions are required to elicit degradation from these cations, making them excellent candidates for implementation as APEs for AEMWEs. When degradation does occur, it is

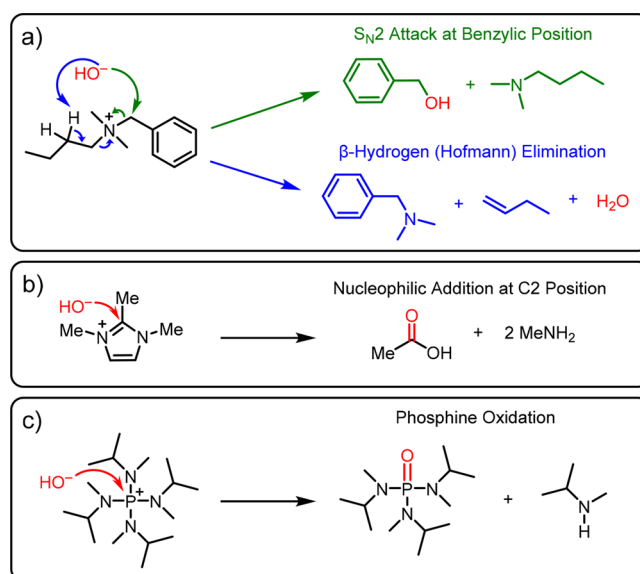


Figure 5. Primary degradation mechanisms for select cations employed in APEs. (a) The two most frequently observed degradation mechanisms for quaternary ammoniums: S_N2 attack and Hofmann elimination. (b) The most common degradation mechanism for less-substituted imidazoliums: nucleophilic addition (S_N2) at the C2 carbon. (c) Most observed degradation mechanism for tetrakis-aminophosphoniums: phosphine oxidation.

mainly through phosphine oxidation (Figure 5c) or Hofmann elimination, depending on the substituents.

While penta-substituted imidazoliums and tetrakis-aminophosphoniums are particularly stable in alkaline conditions, appending them to a polymer backbone to form an APE can be challenging, primarily through postpolymerization functionalization, due to their steric bulk.⁴³ APEs employing bulky cations have demonstrated lower performance due to the low IECs and reduced mechanical integrity. However, high-performance APEs using these cations have been achieved via cross-linking, allowing for higher IECs and improved mechanical properties.⁴⁶ More exploration into the optimal cross-linking conditions is needed to maximize the potential of APEs employing stable yet bulky cations.

The stability of AEMs is often determined via conductivity studies where several testing conditions are commonly employed in the literature, including varying temperatures, hydroxide concentration, vessel, and testing protocols/methods. The degree of variation between/among studies makes comparing results and determining the relative stability of AEMs challenging. Therefore, we propose a procedure to benchmark AEM stability in the community as follows: The desired membrane strips are soaked in 1 M KOH in a polytetrafluoroethylene (PTFE) bottle that has been sealed and placed inside a glass jar sparged with nitrogen, which is then placed in an oven at 80 °C. The combination of PTFE (for the KOH solution) and glass (for containing the PTFE bottle) is critical. PTFE should be used for the KOH solution because hydroxide readily reacts with glass, reducing the pH of the alkaline solution and producing a false positive result of long-term stability,⁶³ and polyethylene is CO_2 -permeable at elevated temperatures,⁶⁴ allowing for carbonate formation and similarly resulting in a lowering of the solution pH. A four-point probe immersed in DI water can be used to measure the conductivity of AEMs; however, this technique can risk

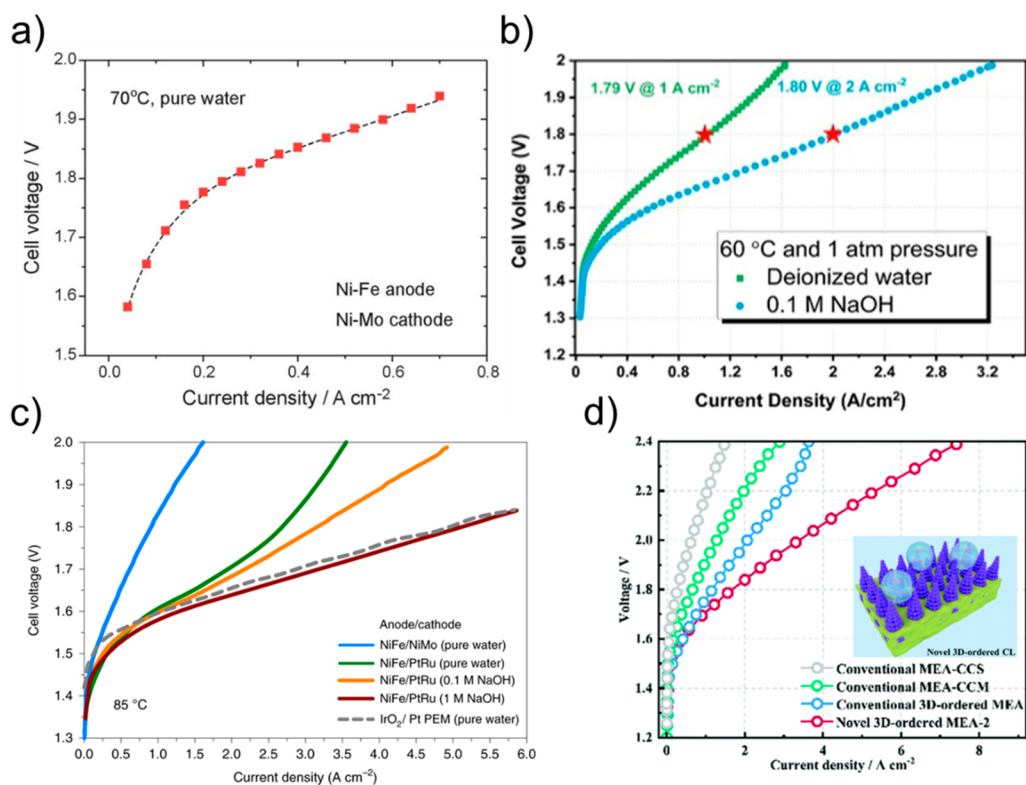


Figure 6. Reported AEMWE performances. (a) First AEMWE reported working in pure water with non-PGM catalysts. (b) Performance difference of AEMWEs using pure water and 0.1 M NaOH. (c) Performance comparison of AEMWEs using Ni-Fe (anode) and Pt-Ru/Ni-Mo (cathode) with pure water and NaOH, and a PEMWE using IrO₂ (anode) and Pt (cathode). (d) Performance of AEMWEs with 3D-ordered MEAs (inset) fabricated using electrochemically deposited VCoP arrays and conventional MEAs, all using pure water. Panel (a) is reprinted with permission from ref 66. Copyright 2012 Royal Society of Chemistry. Panel (b) is reprinted with permission from ref 67. Copyright 2021 American Chemical Society. Panel (c) is reprinted with permission from ref 42. Copyright 2020 Springer Nature. Panel (d) is reprinted with permission from ref 73. Copyright 2022 Royal Society of Chemistry.

carbonation of the membrane during assembly. If possible, a membrane test system⁶⁵ with good control over temperature and atmosphere can be used to obtain more accurate hydroxide ion conductivity values. However, the best way to probe the performance and stability of an AEM is to test it under AEMWE operating conditions in an actual device.

■ AEMWE PERFORMANCE

The realization of the AEMWE and its advantages was historically challenging due to the initial absence of its foundational material, *i.e.*, the APE. In 2012, Xiao et al. produced the first pure-water AEMWE using a self-cross-linking quaternary ammonia polysulfone (*x*QAPS) membrane.⁶⁶ With a Ni-Fe anode and a Ni-Mo cathode, their cell achieved a current density of 0.4 A/cm² at a cell voltage of 1.85 V at 70 °C (Figure 6a). Their work validated the predicted benefits of the AEMWE: the possibility of working with pure water and non-PGM catalysts at both electrodes. Since then, AEMWEs with different APEs and much higher performance have been produced and studied.

Although AEMWEs working with pure water are preferred to reduce/mitigate anticorrosion costs, AEMWEs still perform better with dilute KOH. For example, the AEMWE current density reported by Li et al. was doubled at 1.8 V, from *ca.* 1 A/cm² using pure water to *ca.* 2 A/cm² using 0.1 M NaOH (Figure 6b).⁶⁷ The trend has been frequently reported in the literature: AEMWEs perform significantly better with a dilute (≤ 1 M KOH) alkaline solution supply when compared to pure

water.^{68–71} This phenomenon suggests that the ionic conductivity of present-day APEs is not sufficiently high, thus limiting the overall device performance. Therefore, we believe that developing APEs with higher ionic conductivity and CLs with better transport properties should be the focus for boosting the performance of next-generation AEMWEs. It should also be noted that effectively replacing alkaline solutions with pure water in AEMWEs can take hours before all residual supporting electrolytes are washed away.⁷² Thus, we recommend testing AEMWEs in pure water first. Once again, AEMWEs using pure water are a desirable goal for the future research and development of this technology.

The use of non-PGM catalysts, especially for the anode, is one of the significant advantages of AEMWEs over PEMWEs. Thus, the development of non-PGM OER electrocatalysts has been a critical part of the recent progress in AEMWE performance. For example, Li et al. achieved an AEMWE current density of 2.7 A/cm² at 1.8 V in pure water using Ni-Fe and Pt-Ru as OER and HER electrocatalysts, respectively (Figure 6c).⁴² As expected, the device performance increased by approximately 100%, to 5.3 A/cm², when 1 M NaOH was employed instead of pure water. This performance in 1 M NaOH is comparable to that of state-of-the-art PEMWEs using PGM catalysts. With non-PGM catalysts on both sides of the AEMWE (Ni-Fe for OER and Ni-Mo for HER), they achieved a current density of 0.9 A/cm² at 1.8 V using pure water.⁴² To lower the ion and gas transport resistances, Wan et al. fabricated a 3D-ordered MEA using an electrochemically

deposited VCoP array for both anode and cathode electrodes.⁷³ The thin AEM ($\sim 14 \mu\text{m}$) and ordered CL structure of this 3D-ordered MEA improved the ion and gas transport in the cell. A current density of 4.2 A/cm^2 at 2.0 V was achieved in 1 M KOH , as opposed to *ca.* 1 A/cm^2 using a traditional MEA. With a pure water supply, the electrolyzer generated an outstanding 3.1 A/cm^2 at 2.0 V (Figure 6d). Notably, the performance increase from pure water to 1 M KOH was much smaller (35%) in this case. This further strengthens the arguments in favor of focusing future research on optimizing the APE, as well as the MEA in general. The application of microporous layers and improvements to PTLs may also increase overall AEMWE performance.^{41,74–76}

Recently published AEMWE performance data as a function of the total PGM (Ir, Ru, Pt) catalyst loading are summarized in Figure 7. The current density in this figure was determined

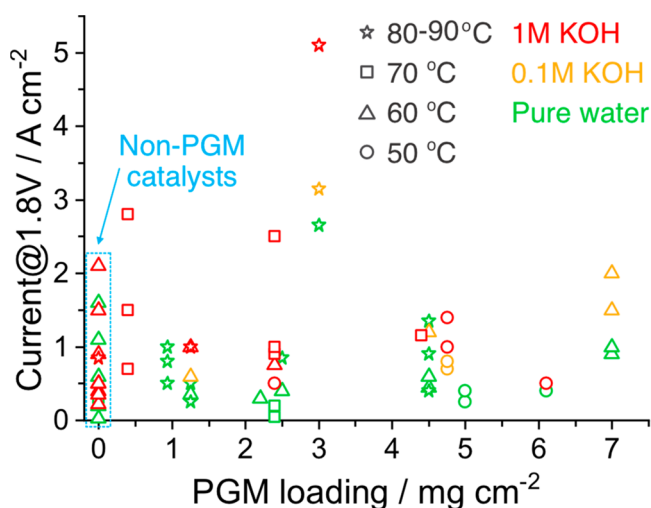


Figure 7. Summary of recently reported AEMWE performances as a function of PGM (Ir, Pt, Ru) catalyst loadings (cathode + anode). Shapes represent different testing temperatures, and colors represent liquid supply. Data extracted from refs 41, 66–70, and 73–76.

at a cell voltage of 1.8 V , which we recommend as the performance metric. At this voltage, a good balance is achieved between high current density and voltage efficiency (68% with respect to the thermodynamic voltage of 1.23 V at $25 \text{ }^\circ\text{C}$). The results for AEMWEs operating with pure water, 0.1 M OH^- , and 1 M OH^- are shown in Figure 7 in green, yellow, and red, respectively. Different electrolyzer temperatures are represented by differently shaped symbols. The data attest to the improvement in the performance of AEMWEs operating with alkaline solutions relative to pure water. While most measured current density values are below 1 A/cm^2 , regardless of PGM loading or solution used, current density values above 2 A/cm^2 are mostly from devices operating in alkaline media. The reported PGM loadings are high, usually above 1 mg/cm^2 , with most devices utilizing Ir-based OER catalysts. Data points for AEMWEs operating with non-PGM catalysts are close to the graph's origin. High performance, above 1.5 A/cm^2 , was nonetheless achieved with several non-PGM catalysts,⁴² attesting to the potential of these catalysts for AEMWE systems. While probing the limits of performance using expensive/rare materials is crucial for understanding and optimizing these systems, there is simply not enough Ir in the crust of the earth to make Ir-based devices economically

feasible at scale. Hence, non-PGM catalysts, especially for the OER, will be the choice for AEMWEs in the long run.

AEMWE OUTLOOK

With the ability to incorporate the advantages of both AWEs and PEMWEs, AEMWEs have the potential to be high-performance and low-cost devices for producing hydrogen (at scale) for a renewable-energy future based on a green hydrogen economy. The advancement of AEMWEs is still in its early stages, but with more attention and effort devoted to this class of electrolyzers in the coming years, progress is imminent. In short, AEMWE performance has increased dramatically, suggesting the potential of AEMWEs to replace AWEs and PEMWEs for large-scale applications. The academic and industrial research roadmap for the future of AEMWEs should include: (1) design and synthesis of APEs with high IECs and mechanical stability to narrow/close the gap between dilute alkaline and pure water AEMWEs; (2) standardization of electrocatalyst testing and performance metrics as well as the complete elimination of PGM electrocatalysts from AEMWEs; (3) testing of dilute-alkaline and pure-water AEMWE systems with the goal of optimizing electrolyzers operating using pure water; and (4) assuring high stability of AEMWE operation on a multiyear time scale. Standard accelerated stress test protocols for AEMWEs need to be developed soon. We stress the importance of using performance metrics such as the current density of an AEMWE at 1.8 V and not over-relying on CP RDE experiments. This roadmap will require developing better APE materials and HER/OER electrocatalysts, a better integration of the electrolyzer components, and a deeper understanding of the physicochemical phenomena within AEMWEs. With more efforts directed into these areas, we are confident that AEMWEs will soon reach the next development stage and flourish into a productive and essential energy discipline.

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Notes

The authors declare no competing financial interest.

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ACKNOWLEDGMENTS

Research primarily supported as part of the Center for Alkaline Based Energy Solutions (CABES), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under award DE-SC0019445. L.Q. acknowledges support by the New York State Energy Research and Development Authority (NYSERDA) under agreement 146218. A.M.V. acknowledges support by the National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP) grant DGE-1650441 and the Cornell Dean's Excellence Scholarship. M.-J.K. acknowledges support by the National Research Foundation of Korea (NRF) grant NRF-2021R1A2C1010698, funded by the Korean government. J.S. acknowledges support by the Cornell Energy Systems Institute (CESI) and the Kavli Institute at Cornell (KIC). L.X. and L.Z. acknowledge support by the National Natural Science Foundation of China (NSFC) grants 21991154, 21991150, and 22122204, and the Fundamental Research Funds for the Central Universities grant 2042022kf1174.

REFERENCES

- (1) U.S. Department of Energy. *Hydrogen production: Natural gas reforming*, 2022. <https://www.energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming> (accessed 03/01/2023).
- (2) Buttler, A.; Spliethoff, H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. *Renew. Sust. Energy Rev.* **2018**, *82*, 2440–2454.
- (3) Haug, P.; Koj, M.; Turek, T. Influence of process conditions on gas purity in alkaline water electrolysis. *Int. J. Hydrog. Energy* **2017**, *42* (15), 9406–9418.
- (4) Pham, C. V.; Escalera-López, D.; Mayrhofer, K.; Cherevko, S.; Thiele, S. Essentials of High Performance Water Electrolyzers—From Catalyst Layer Materials to Electrode Engineering. *Adv. Energy Mater.* **2021**, *11* (44), 2101998.
- (5) Raja Sulaiman, R. R.; Wong, W. Y.; Loh, K. S. Recent developments on transition metal-based electrocatalysts for application in anion exchange membrane water electrolysis. *Int. J. Energy Res.* **2022**, *46* (3), 2241–2276.
- (6) *Daily Metal Prices*. <https://www.dailymetalprice.com/> (accessed).
- (7) Chen, F.-Y.; Wu, Z.-Y.; Adler, Z.; Wang, H. Stability challenges of electrocatalytic oxygen evolution reaction: From mechanistic understanding to reactor design. *Joule* **2021**, *5* (7), 1704–1731.
- (8) Zhou, J.; Zhang, L.; Huang, Y.-C.; Dong, C.-L.; Lin, H.-J.; Chen, C.-T.; Tjeng, L.; Hu, Z. Voltage- and time-dependent valence state transition in cobalt oxide catalysts during the oxygen evolution reaction. *Nat. Commun.* **2020**, *11* (1), 1–10.
- (9) Cherevko, S.; Zeradjanin, A. R.; Topalov, A. A.; Kulyk, N.; Katsounaros, I.; Mayrhofer, K. J. Dissolution of noble metals during oxygen evolution in acidic media. *ChemCatChem*. **2014**, *6* (8), 2219–2223.
- (10) Stoerzinger, K. A.; Diaz-Morales, O.; Kolb, M.; Rao, R. R.; Frydendal, R.; Qiao, L.; Wang, X. R.; Halck, N. B.; Rossmeisl, J.; Hansen, H. A.; et al. Orientation-Dependent Oxygen Evolution on RuO₂ without Lattice Exchange. *ACS Energy Lett.* **2017**, *2* (4), 876–881.

- (11) Wang, C.; Qi, L. Heterostructured Inter-Doped Ruthenium–Cobalt Oxide Hollow Nanosheets for Highly Efficient Overall Water Splitting. *Angew. Chem., Int. Ed.* **2020**, *132* (39), 17372–17377.
- (12) Wang, H.; Yang, Y.; DiSalvo, F. J.; Abruña, H. D. Multifunctional Electrocatalysts: Ru–M (M = Co, Ni, Fe) for Alkaline Fuel Cells and Electrolyzers. *ACS Catal.* **2020**, *10* (8), 4608–4616.
- (13) Wang, S.; Xu, B.; Huo, W.; Feng, H.; Zhou, X.; Fang, F.; Xie, Z.; Shang, J. K.; Jiang, J. Efficient FeCoNiCuPd thin-film electrocatalyst for alkaline oxygen and hydrogen evolution reactions. *Appl. Catal. B: Environ.* **2022**, *313*, 121472.
- (14) Lee, J.; Kumar, A.; Yang, T.; Liu, X.; Jadhav, A. R.; Park, G. H.; Hwang, Y.; Yu, J.; Nguyen, C. T.; Liu, Y.; et al. Stabilizing the OOH* intermediate via pre-adsorbed surface oxygen of a single Ru atom-bimetallic alloy for ultralow overpotential oxygen generation. *Energy Environ. Sci.* **2020**, *13* (12), S152–S164.
- (15) Duan, R.; Li, Y.; Wang, S.; Gong, J.; Tong, Y.; Qi, W. Fast and deep reconstruction of coprecipitated Fe phosphates on nickel foams for an alkaline oxygen evolution reaction. *J. Phys. Chem. Lett.* **2022**, *13* (6), 1446–1452.
- (16) Shin, S.; Kwon, T.; Kim, K.; Kim, M.; Kim, M. H.; Lee, Y. Single-Phase Perovskite SrIrO₃ Nanofibers as a Highly Efficient Electrocatalyst for a pH-Universal Oxygen Evolution Reaction. *ACS Appl. Energy Mater.* **2022**, *5*, 6146–6154.
- (17) Walter, C.; Kalra, S.; Beltrán-Suito, R.; Schwarze, M.; Menezes, P.; Driess, M. Manganese sulfide enables the formation of a highly active β-MnOOH electrocatalyst for effective alkaline water oxidation. *Materials Today Chemistry* **2022**, *24*, 100905.
- (18) Yuan, G.; Bai, J.; Zhang, L.; Chen, X.; Ren, L. The effect of P vacancies on the activity of cobalt phosphide nanorods as oxygen evolution electrocatalyst in alkali. *Appl. Catal. B: Environ.* **2021**, *284*, 119693.
- (19) Kaur, G.; Biswas, R.; Haldar, K. K.; Sen, T. DNA Origami-Templated Bimetallic Core–Shell Nanostructures for Enhanced Oxygen Evolution Reaction. *J. Phys. Chem. C* **2022**, *126* (16), 6915–6924.
- (20) McCrory, C. C.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135* (45), 16977–16987.
- (21) Zahran, Z. N.; Mohamed, E. A.; Tsubonouchi, Y.; Ishizaki, M.; Togashi, T.; Kurihara, M.; Saito, K.; Yui, T.; Yagi, M. Electrocatalytic water splitting with unprecedentedly low overpotentials by nickel sulfide nanowires stuffed into carbon nitride scabbards. *Energy Environ. Sci.* **2021**, *14* (10), 5358–5365.
- (22) Dong, B.; Zhao, X.; Han, G.-Q.; Li, X.; Shang, X.; Liu, Y.-R.; Hu, W.-H.; Chai, Y.-M.; Zhao, H.; Liu, C.-G. Two-step synthesis of binary Ni–Fe sulfides supported on nickel foam as highly efficient electrocatalysts for the oxygen evolution reaction. *J. Mater. Chem. A* **2016**, *4* (35), 13499–13508.
- (23) Zhang, B.; Wang, L.; Cao, Z.; Kozlov, S. M.; García de Arquer, F. P.; Dinh, C. T.; Li, J.; Wang, Z.; Zheng, X.; Zhang, L.; et al. High-valence metals improve oxygen evolution reaction performance by modulating 3d metal oxidation cycle energetics. *Nat. Catal.* **2020**, *3* (12), 985–992.
- (24) Zhang, W.; Chen, G.; Du, Y.; Zhu, S.; Zhang, J.; Liu, G.; Zhang, F.; Wang, S.; Wang, X. Large-Scale Synthesis of Fe-Doped Amorphous Cobalt Oxide Electrocatalysts at Room Temperature for the Oxygen Evolution Reaction. *ACS Appl. Energy Mater.* **2022**, *5* (3), 3129–3136.
- (25) Lei, C.; Yang, K.; Wang, G.; Wang, G.; Lu, J.; Xiao, L.; Zhuang, L. Impact of Catalyst Reconstruction on the Durability of Anion Exchange Membrane Water Electrolysis. *ACS Sustainable Chem. Eng.* **2022**, *10*, 16725.
- (26) Garsany, Y.; Singer, I. L.; Swider-Lyons, K. E. Impact of film drying procedures on RDE characterization of Pt/VC electrocatalysts. *J. Electroanal. Chem.* **2011**, *662* (2), 396–406.
- (27) Xu, D.; Stevens, M. B.; Cosby, M. R.; Oener, S. Z.; Smith, A. M.; Enman, L. J.; Ayers, K. E.; Capuano, C. B.; Renner, J. N.; Danilovic, N.; et al. Earth-abundant oxygen electrocatalysts for alkaline anion-exchange-membrane water electrolysis: Effects of catalyst conductivity and comparison with performance in three-electrode cells. *ACS Catal.* **2019**, *9* (1), 7–15.
- (28) Yu, L.; Ren, Z. Systematic study of the influence of iR compensation on water electrolysis. *Materials Today Physics* **2020**, *14*, 100253.
- (29) Anantharaj, S.; Ede, S.; Karthick, K.; Sankar, S. S.; Sangeetha, K.; Karthik, P.; Kundu, S. Precision and correctness in the evaluation of electrocatalytic water splitting: revisiting activity parameters with a critical assessment. *Energy Environ. Sci.* **2018**, *11* (4), 744–771.
- (30) Bera, K.; Karmakar, A.; Kumaravel, S.; Sam Sankar, S.; Madhu, R.; N Dhandapani, H.; Nagappan, S.; Kundu, S. Vanadium-doped nickel cobalt layered double hydroxide: A high-performance oxygen evolution reaction electrocatalyst in alkaline medium. *Inorg. Chem.* **2022**, *61* (10), 4502–4512.
- (31) Tovini, M. F.; Hartig-Weiß, A.; Gasteiger, H. A.; El-Sayed, H. A. The discrepancy in oxygen evolution reaction catalyst lifetime explained: RDE vs MEA-dynamicity within the catalyst layer matters. *J. Electrochem. Soc.* **2021**, *168* (1), 014512.
- (32) Hartig-Weiss, A.; Tovini, M. F.; Gasteiger, H. A.; El-Sayed, H. A. OER catalyst durability tests using the rotating disk electrode technique: the reason why this leads to erroneous conclusions. *ACS Appl. Energy Mater.* **2020**, *3* (11), 10323–10327.
- (33) McCrory, C. C.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices. *J. Am. Chem. Soc.* **2015**, *137* (13), 4347–4357.
- (34) You, W.; Noonan, K. J. T.; Coates, G. W. Alkaline-stable anion exchange membranes: A review of synthetic approaches. *Prog. Polym. Sci.* **2020**, *100*, 101177.
- (35) Park, H. J.; Chu, X.; Kim, S. P.; Choi, D.; Jung, J. W.; Woo, J.; Baek, S. Y.; Yoo, S. J.; Chung, Y.-C.; Seong, J. G.; et al. Effect of N-cyclic cationic groups in poly (phenylene oxide)-based catalyst ionomer membranes for anion exchange membrane fuel cells. *J. Membr. Sci.* **2020**, *608*, 118183.
- (36) Leng, Y.; Chen, G.; Mendoza, A. J.; Tighe, T. B.; Hickner, M. A.; Wang, C. Y. Solid-state water electrolysis with an alkaline membrane. *J. Am. Chem. Soc.* **2012**, *134* (22), 9054–9057.
- (37) Pan, Y.; Zhang, Q.; Yan, X.; Liu, J.; Xu, X.; Wang, T.; El Hamouti, I.; Ruan, X.; Hao, C.; He, G. Hydrophilic side chain assisting continuous ion-conducting channels for anion exchange membranes. *J. Membr. Sci.* **2018**, *552*, 286–294.
- (38) Peng, H.; Li, Q.; Hu, M.; Xiao, L.; Lu, J.; Zhuang, L. Alkaline polymer electrolyte fuel cells stably working at 80 °C. *J. Power Sources* **2018**, *390*, 165–167.
- (39) Lee, W.-H.; Park, E. J.; Han, J.; Shin, D. W.; Kim, Y. S.; Bae, C. Poly(terphenylene) Anion Exchange Membranes: The Effect of Backbone Structure on Morphology and Membrane Property. *ACS Macro Lett.* **2017**, *6* (5), 566–570.
- (40) Pan, D.; Olsson, J. S.; Jannasch, P. Poly (fluorene alkylene) Anion Exchange Membranes with Pendant Spirocyclic and Bis-Spirocyclic Quaternary Ammonium Cations. *ACS Appl. Energy Mater.* **2022**, *5* (1), 981–991.
- (41) Soni, R.; Miyaniishi, S.; Kuroki, H.; Yamaguchi, T. Pure Water Solid Alkaline Water Electrolyzer Using Fully Aromatic and High-Molecular-Weight Poly(fluorene-alt-tetrafluorophenylene)-trimethyl Ammonium Anion Exchange Membranes and Ionomers. *ACS Appl. Energy Mater.* **2021**, *4* (2), 1053–1058.
- (42) Li, D.; Park, E. J.; Zhu, W.; Shi, Q.; Zhou, Y.; Tian, H.; Lin, Y.; Serov, A.; Zulevi, B.; Baca, E. D.; et al. Highly quaternized polystyrene ionomers for high performance anion exchange membrane water electrolyzers. *Nat. Energy* **2020**, *5* (5), 378–385.
- (43) Selhorst, R.; Gaitor, J.; Lee, M.; Markovich, D.; Yu, Y.; Treichel, M.; Olavarria Gallegos, C.; Kowalewski, T.; Kourkoutis, L. F.; Hayward, R. C.; et al. Multiblock copolymer anion-exchange membranes derived from vinyl addition polynorbornenes. *ACS Appl. Energy Mater.* **2021**, *4* (9), 10273–10279.
- (44) Mandal, M.; Huang, G.; Kohl, P. A. Highly Conductive Anion-Exchange Membranes Based on Cross-Linked Poly(norbornene):

- Vinyl Addition Polymerization. *ACS Appl. Energy Mater.* **2019**, *2* (4), 2447–2457.
- (45) Chen, W.; Mandal, M.; Huang, G.; Wu, X.; He, G.; Kohl, P. A. Highly Conducting Anion-Exchange Membranes Based on Cross-Linked Poly(norbornene): Ring Opening Metathesis Polymerization. *ACS Appl. Energy Mater.* **2019**, *2* (4), 2458–2468.
- (46) You, W.; Padgett, E.; MacMillan, S. N.; Muller, D. A.; Coates, G. W. Highly conductive and chemically stable alkaline anion exchange membranes via ROMP of trans-cyclooctene derivatives. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116* (20), 9729–9734.
- (47) You, W.; Ganley, J. M.; Ernst, B. G.; Peltier, C. R.; Ko, H.-Y.; DiStasio, R. A.; Knowles, R. R.; Coates, G. W. Expedient synthesis of aromatic-free piperidinium-functionalized polyethylene as alkaline anion exchange membranes. *Chem. Sci.* **2021**, *12* (11), 3898–3910.
- (48) Trant, C.; Hwang, S.; Bae, C.; Lee, S. Synthesis and characterization of anion-exchange membranes using semicrystalline triblock copolymers in ordered and disordered states. *Macromolecules* **2020**, *53* (19), 8548–8561.
- (49) Zeng, L.; Yuan, W.; Ma, X.; He, Q.; Zhang, L.; Wang, J.; Wei, Z. Dual-Cation Interpenetrating Polymer Network Anion Exchange Membrane for Fuel Cells and Water Electrolyzers. *Macromolecules* **2022**, *55*, 4647–4655.
- (50) Dang, H.-S.; Jannasch, P. Exploring different cationic alkyl side chain designs for enhanced alkaline stability and hydroxide ion conductivity of anion-exchange membranes. *Macromolecules* **2015**, *48* (16), 5742–5751.
- (51) Mohanty, A. D.; Tignor, S. E.; Krause, J. A.; Choe, Y.-K.; Bae, C. Systematic alkaline stability study of polymer backbones for anion exchange membrane applications. *Macromolecules* **2016**, *49* (9), 3361–3372.
- (52) Miyanishi, S.; Yamaguchi, T. Highly conductive mechanically robust high M_w polyfluorene anion exchange membrane for alkaline fuel cell and water electrolysis application. *Polym. Chem.* **2020**, *11* (23), 3812–3820.
- (53) Matanovic, I.; Maurya, S.; Park, E. J.; Jeon, J. Y.; Bae, C.; Kim, Y. S. Adsorption of Polyaromatic Backbone Impacts the Performance of Anion Exchange Membrane Fuel Cells. *Chem. Mater.* **2019**, *31* (11), 4195–4204.
- (54) Maurya, S.; Lee, A. S.; Li, D.; Park, E. J.; Leonard, D. P.; Noh, S.; Bae, C.; Kim, Y. S. On the origin of permanent performance loss of anion exchange membrane fuel cells: Electrochemical oxidation of phenyl group. *J. Power Sources* **2019**, *436*, 226866.
- (55) Li, D.; Matanovic, I.; Lee, A. S.; Park, E. J.; Fujimoto, C.; Chung, H. T.; Kim, Y. S. Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer. *ACS Appl. Mater. Interfaces* **2019**, *11* (10), 9696–9701.
- (56) Li, D.; Motz, A. R.; Bae, C.; Fujimoto, C.; Yang, G.; Zhang, F.-Y.; Ayers, K. E.; Kim, Y. S. Durability of anion exchange membrane water electrolyzers. *Energy Environ. Sci.* **2021**, *14* (6), 3393–3419.
- (57) Yang, Y.; Peltier, C. R.; Zeng, R.; Schimmenti, R.; Li, Q.; Huang, X.; Yan, Z.; Potsi, G.; Selhorst, R.; Lu, X.; et al. Electrocatalysis in Alkaline Media and Alkaline Membrane-Based Energy Technologies. *Chem. Rev.* **2022**, *122* (6), 6117–6321.
- (58) You, W.; Hugar, K. M.; Selhorst, R. C.; Treichel, M.; Peltier, C. R.; Noonan, K. J. T.; Coates, G. W. Degradation of Organic Cations under Alkaline Conditions. *J. Org. Chem.* **2021**, *86* (1), 254–263.
- (59) Marino, M.; Kreuer, K. Alkaline stability of quaternary ammonium cations for alkaline fuel cell membranes and ionic liquids. *ChemSusChem* **2015**, *8* (3), 513–523.
- (60) Pan, D.; Bakvand, P. M.; Pham, T. H.; Jannasch, P. Improving poly(arylene piperidinium) anion exchange membranes by monomer design. *J. Mater. Chem. A* **2022**, *10* (31), 16478–16489.
- (61) Hugar, K. M.; Kostalik, H. A., IV; Coates, G. W. Imidazolium cations with exceptional alkaline stability: a systematic study of structure–stability relationships. *J. Am. Chem. Soc.* **2015**, *137* (27), 8730–8737.
- (62) Womble, C. T.; Kang, J.; Hugar, K. M.; Coates, G. W.; Bernhard, S.; Noonan, K. J. Rapid analysis of tetrakis (dialkylamino) phosphonium stability in alkaline media. *Organometallics* **2017**, *36* (20), 4038–4046.
- (63) Sturgeon, M. R.; Macomber, C. S.; Engtrakul, C.; Long, H.; Pivovar, B. S. Hydroxide based benzyltrimethylammonium degradation: Quantification of rates and degradation technique development. *J. Electrochem. Soc.* **2015**, *162* (4), F366.
- (64) Li, H.; Yang, D.; Zhang, D.; Zhu, Y.; Ge, P.; Qi, D.; Zhang, Z. Permeation Characteristic and Mechanism of CO₂ in High Density Polyethylene. In *Chinese Materials Conference, 2017*; Springer; pp 963–973.
- (65) Ziv, N.; Dekel, D. R. A practical method for measuring the true hydroxide conductivity of anion exchange membranes. *Electrochem. Commun.* **2018**, *88*, 109–113.
- (66) Xiao, L.; Zhang, S.; Pan, J.; Yang, C.; He, M.; Zhuang, L.; Lu, J. First implementation of alkaline polymer electrolyte water electrolysis working only with pure water. *Energy Environ. Sci.* **2012**, *5* (7), 7869–7871.
- (67) Li, K.; Yu, S.; Li, D.; Ding, L.; Wang, W.; Xie, Z.; Park, E. J.; Fujimoto, C.; Cullen, D. A.; Kim, Y. S.; et al. Engineered Thin Diffusion Layers for Anion-Exchange Membrane Electrolyzer Cells with Outstanding Performance. *ACS Appl. Mater. Interfaces* **2021**, *13* (43), 50957–50964.
- (68) Park, J. E.; Kang, S. Y.; Oh, S.-H.; Kim, J. K.; Lim, M. S.; Ahn, C.-Y.; Cho, Y.-H.; Sung, Y.-E. High-performance anion-exchange membrane water electrolysis. *Electrochim. Acta* **2019**, *295*, 99–106.
- (69) Fortin, P.; Khoza, T.; Cao, X.; Martinsen, S. Y.; Barnett, A. O.; Holdcroft, S. High-performance alkaline water electrolysis using Aemion anion exchange membranes. *J. Power Sources* **2020**, *451*, 227814.
- (70) Chen, N.; Paek, S. Y.; Lee, J. Y.; Park, J. H.; Lee, S. Y.; Lee, Y. M. High-performance anion exchange membrane water electrolyzers with a current density of 7.68 A cm⁻² and durability of 1000 h. *Energy Environ. Sci.* **2021**, *14* (12), 6338–6348.
- (71) Wang, L.; Weissbach, T.; Reissner, R.; Ansar, A.; Gago, A. S.; Holdcroft, S.; Friedrich, K. A. High Performance Anion Exchange Membrane Electrolysis Using Plasma-Sprayed, Non-Precious-Metal Electrodes. *ACS Appl. Energy Mater.* **2019**, *2* (11), 7903–7912.
- (72) Hassan, N. U.; Zheng, Y.; Kohl, P. A.; Mustain, W. E. KOH vs Deionized Water Operation in Anion Exchange Membrane Electrolyzers. *J. Electrochem. Soc.* **2022**, *169* (4), 044526.
- (73) Wan, L.; Xu, Z.; Xu, Q.; Wang, P.; Wang, B. Overall design of novel 3D-ordered MEA with drastically enhanced mass transport for alkaline electrolyzers. *Energy Environ. Sci.* **2022**, *15* (5), 1882–1892.
- (74) Xiao, J.; Oliveira, A. M.; Wang, L.; Zhao, Y.; Wang, T.; Wang, J.; Setzler, B. P.; Yan, Y. Water-Fed Hydroxide Exchange Membrane Electrolyzer Enabled by a Fluoride-Incorporated Nickel–Iron Oxyhydroxide Oxygen Evolution Electrode. *ACS Catal.* **2021**, *11* (1), 264–270.
- (75) Liu, J.; Kang, Z.; Li, D.; Pak, M.; Alia, S. M.; Fujimoto, C.; Bender, G.; Kim, Y. S.; Weber, A. Z. Elucidating the Role of Hydroxide Electrolyte on Anion-Exchange-Membrane Water Electrolyzer Performance. *J. Electrochem. Soc.* **2021**, *168* (5), 054522.
- (76) Razmjooei, F.; Morawietz, T.; Taghizadeh, E.; Hadjixenophontos, E.; Mues, L.; Gerle, M.; Wood, B. D.; Harms, C.; Gago, A. S.; Ansar, S. A.; et al. Increasing the performance of an anion-exchange membrane electrolyzer operating in pure water with a nickel-based microporous layer. *Joule* **2021**, *5* (7), 1776–1799.

NOTE ADDED AFTER ASAP PUBLICATION

This paper published ASAP on March 28, 2023. Additional minor text changes were received and a change to an author's affiliation was made. The corrected version was reposted April 5, 2023.